

# PATENT ABSTRACTS OF JAPAN

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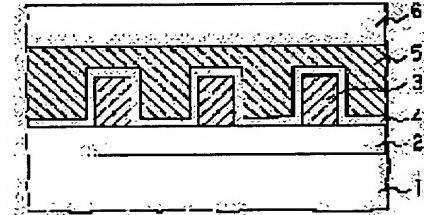
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## (54) FORMING METHOD OF INSULATING FILM

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To enable insulating film to be stabilized for a long term without causing a void by laminating insulating films made of an organic material on the surface of silicon oxide films after feeding silane coupling agent.

**SOLUTION:** Firstly, the first silicon oxide film 2 is formed on a silicon substrate 1 and after the formation of a wiring pattern 3, the second silicon oxide film 4 is formed. Next, a wafer is spin coated with carbon tetrachloride melted with one wt.% of silane coupling agent. Thus, silane coupling agent is chemically coupled with hydroxyl group on the silicon oxide film surface. Next, an organic insulating film 5 made of amorphous teflon is formed. Later, the third silicon oxide film 6 is formed. In such a constitution, the laminated layer films made of the second silicon oxide film 4, the organic insulating film 5 and the third silicon oxide film 6 are formed into an interlayer insulating film at low dielectric constant due to the existance of the organic insulating film 5.



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**CLAIMS****[Claim(s)]**

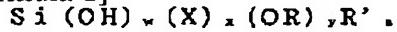
[Claim 1] The formation approach of the insulator layer characterized by carrying out the laminating of the insulator layer which consists of an organic material after making a silane coupling agent hold on the front face of the silicon oxide film.

[Claim 2] The formation approach of the insulator layer characterized by carrying out the laminating of the insulator layer which consists of an organic material after hydroxyl-group-izing the front face of the silicon oxide film.

[Claim 3] The formation approach of the insulator layer according to claim 1 characterized by hydroxyl-group-izing the front face of said silicon oxide film before making said silane coupling agent hold.

[Claim 4] The formation approach of the insulator layer according to claim 1 characterized by heating after making said silane coupling agent hold.

[Claim 5] The formation approach of the insulator layer according to claim 1 characterized by using the compound shown in \*\* 1 as said silane coupling agent.

**[Formula 1]**

(但し、w、x、y、zは整数であり、 $0 \leq w \leq 3$ 、 $0 \leq x \leq 3$ 、 $0 \leq y \leq 3$ 、 $1 \leq z \leq 3$

$w+x+y \geq 1$ 、 $w+x+y+z=4$ を満たす。

また、Xはハロゲン、ORはアルコキシリル基を示す。

R'はアルキル基、ハロゲン化アルキル基、アルケン基、アミノアルキル基およびこれらの誘導体

より選ばれるいずれか1種を示し、z $\geq 2$ のときは、これらの任意の組合せとする。)

[Claim 6] The formation approach of the insulator layer according to claim 5 characterized by consisting of a compound of R' in the above-izing 1 with which either contains a fluorine atom at least, and said organic material contains a fluorine atom.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]**

[0001]

[Field of the Invention] This invention relates to the formation approach of the insulator layer which carries out the laminating of the insulator layer which consists of an organic material on the silicon oxide film.

[0002]

[Description of the Prior Art] In the manufacture process of a semiconductor device, the organic material film has been conventionally used as a resist mask the object for patterning of the predetermined ingredient film, and for ion implantations.

[0003] Moreover, by recent years, in order to reduce the wiring capacity actualized with detailed-izing of a semiconductor device, low dielectric constant-ization of an interlayer insulation film is called for, by the inorganic material film, obtaining considers as the ingredient film which can attain a difficult low dielectric constant, and the organic material film attracts attention.

[0004] SiO<sub>2</sub> conventionally used as an interlayer insulation film Membranous specific inductive capacity is 3.9 and the specific inductive capacity of 3.5-3.0, and the fluororesin film of the specific inductive capacity of the polyimide system resin film is dramatically as low as 2.5-1.9 to the specific inductive capacity of the SiOF film being 3.7-3.2. For this reason, using the interlayer insulation film with which a design rule consists of such organic material film in a semiconductor device 0.18 micrometers or less is examined.

[0005]

[Problem(s) to be Solved by the Invention] By the way, when the organic material film was used as a resist mask, since this organic material film was what is removed at the time of completion of a semiconductor device, an adhesive property with the ingredient film used as a substrate was not asked for long-term dependability. However, since this organic material film will remain at the time of completion of a semiconductor device when using the organic material film as an interlayer insulation film, it is necessary to have covered the ingredient film used as a substrate at the long period of time, and to have pasted stability. It is because it originates in this that an adhesive property with the ingredient film used as the organic material film and a substrate is inadequate and becomes easy to produce a defect in a semiconductor device.

[0006] In forming the insulator layer which consists of fluororesin especially on the silicon oxide film, both adhesive property serves as imperfection. Moreover, when the silicon oxide film used as a substrate has detailed irregularity, it also becomes difficult to fully embed the inside of a crevice by the insulator layer which consists of this fluororesin.

[0007] In order to form an interlayer insulation film in drawing 2 so that the circuit pattern 103 formed on the 1st silicon oxide film 102 on a silicon substrate 101 may be covered, the wafer which carried out the laminating of the 2nd silicon oxide film 104, the organic compound insulator 105 which consists of fluororesin, and the 3rd silicon oxide film 106 is shown. What is necessary is to apply the coating made to dissolve fluororesin in a solvent, and for heat treatment in the temperature region more than glass transition temperature just to remove a solvent, after forming the 2nd silicon oxide film 104, in order to form the organic compound insulator 105 which consists of fluororesin. However, the organic compound insulator 105 formed actually will become what has a void 107 between circuit patterns 103. This is because the coefficient of thermal expansion of fluororesin more than glass transition temperature is very large, so a big volume change is caused at the time of heat treatment for solvent clearance.

[0008] Without producing a void on the silicon oxide film in this invention in view of this conventional actual

condition, it continues at a long period of time, and aims at offering the formation approach of the insulator layer which forms the insulator layer which consists of an organic material so that it can be made to exist in stability.

[0009]

[Means for Solving the Problem] After the formation approach of the insulator layer concerning this invention attains the above-mentioned object and makes a silane coupling agent hold on the front face of the silicon oxide film, it carries out the laminating of the insulator layer (an organic compound insulator is called hereafter.) which consists of an organic material.

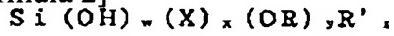
[0010] Moreover, after hydroxyl-group-izing the front face of the silicon oxide film, the above-mentioned object can be attained also by carrying out the laminating of the organic compound insulator.

[0011] Furthermore, if a hydroxyl group and a silane coupling agent are made to react by making a silane coupling agent hold after hydroxyl-group-izing the front face of the silicon oxide film, further adhesive improvement with the silicon oxide film and an organic compound insulator can be aimed at. In this case, it heats if needed and is suitable after making a silane coupling agent hold on the silicon oxide film. Thereby, the reaction of the functional group in a silane coupling agent and the hydroxyl group of a silicon oxide film front face can be promoted.

[0012] By the way, as a silane coupling agent, it is suitable using the compound shown in \*\* 2.

[0013]

[Formula 2]



(但し、w、x、y、zは整数であり、 $0 \leq w \leq 3$ 、 $0 \leq x \leq 3$ 、 $0 \leq y \leq 3$ 、 $1 \leq z \leq 3$

$w+x+y \geq 1$ 、 $w+x+y+z=4$ を満たす。

また、Xはハロゲン、ORはアルコキシル基を示す。

R'はアルキル基、ハロゲン化アルキル基、アルケン基、アミノアルキル基およびこれらの誘導体

より選ばれるいざれか1種を示し、 $z \geq 2$ のときは、これらの任意の組合わせとする。)

[0014] In the compound shown in this \*\* 2, the hydroxyl group shown by OH, the alkoxy group shown by OR, and the halogen shown by X react with the hydroxyl group (-OH) of a silicon oxide film front face, and bears the role which combines the silicon oxide film and a silane coupling agent. For this reason, as for at least one of four joint hands which Si atom has, what is been a hydroxyl group, an alkoxy group, or a halogen (that is, they are the inside of \*\* 2 and  $w+x+y>=1$ ) is desirable. In addition, two or more kinds in a hydroxyl group, an alkoxy group, and a halogen may combine with common Si atom.

[0015] On the other hand, the alkyl group shown by R', an alkyl halide radical, an alkene radical, amino alkyl groups, and these derivatives bear adsorption with the organic compound insulator formed behind. For this reason, as for at least one of four joint hands which Si atom has, what is combined with these substituents (that is, they are the inside of \*\* 2 and  $z>=1$ ) is desirable. In addition, when two or more R' has combined with common Si atom, in [ namely, when / among \*\* 2 when it is  $z>=2$  ], even if R' is the substituents which have the same structure, they may be substituents which have structure different, respectively.

[0016] Moreover, since the compound (fluororesin is called hereafter.) containing a fluorine atom can control this diffusion of Cu especially as an organic material for forming an organic compound insulator when specific inductive capacity is not only dramatically low, but Cu is used as a wiring material although not limited, the application as an interlayer insulation film is expected.

[0017] It is suitable using what faces forming the organic compound insulator which consists of this fluororesin, and contains a fluorine atom as a silane coupling agent. That is, among \*\* 2, the halogen shown by X shall be used as a fluorine atom, or at least one of the R' shall contain a fluorine atom, and it is suitable. A fluorine atom may be introduced into an alkene radical, amino alkyl groups, or these derivatives even if R' is the alkyl halide radical into which the fluorine atom was introduced as a halogen in the case of the latter.

[0018] If this invention is applied, the adhesive property of the silicon oxide film and an organic compound insulator can be raised. Moreover, when forming the fluororesin film as an organic compound insulator, much more adhesive improvement can be aimed at by using the silane coupling agent which contains a fluorine atom

as mentioned above.

[0019]

[Embodiment of the Invention] Hereafter, the gestalt of the concrete operation which applied this invention is explained.

[0020] the gestalt of the 1st operation -- here, after hydroxyl-group-izing the front face of the silicon oxide film formed evenly and applying a silane coupling agent, the example which forms an organic compound insulator is explained.

[0021] First, prepared the wafer formed on the flat substrate at the thickness which 0.5 micrometers of silicon oxide film become, this wafer was made to lay in a dry etching system, and plasma treatment of the silicon oxide film front face was carried out on condition that the following.

[0022]

#### プラズマ処理条件

導入ガス : Ar 流量 200 sccm  
               H<sub>2</sub> 流量 50 sccm  
               圧力 : 13.3 Pa  
               RF電力 : 200W (13.56MHz)  
               ウェハ温度 : 室温

Thereby, Si-O association of a silicon oxide film front face was hydroxyl-group-ized, and became Si-OH.

[0023] Next, as a silane coupling agent, trimethylchlorosilane (CH<sub>3</sub>)<sub>3</sub>SiCl was prepared, the spin coat of what dissolved this in the carbon tetrachloride 1% of the weight was carried out to the above-mentioned wafer, and it was left at the room temperature for about 1 hour. In addition, thereby, trimethylchlorosilane carried out the chemical bond to the hydroxyl group of a silicon oxide film front face.

[0024] Then, the carbon tetrachloride washed this wafer and superfluous unreacted trimethylchlorosilane was removed. This obtained the wafer with which the surface treatment of the silicon oxide film was made.

[0025] And the organic compound insulator which consists of polymethylmethacrylate of the Polyscience molecular weight 100000 was formed at the thickness it is thin about 1 micrometer on the silicon oxide film with which surface treatment was performed as mentioned above. In addition, in order to form this organic compound insulator, to prepare the 2-% of the weight chloroform solution of the above-mentioned polymethylmethacrylate, to apply this with a spin coat method on the above-mentioned silicon oxide film and to fully remove the solvent in the film after that, it was made to dry at 50 degrees C for 3 hours using a vacuum dryer.

[0026] In the gestalt of this operation, since the organic compound insulator is formed through the silane coupling agent on the silicon oxide film, the adhesive property of the silicon oxide film and an organic compound insulator is large.

[0027] the gestalt of the 2nd operation -- here, the example which forms an organic compound insulator in the front face of the silicon oxide film thinly formed so that a circuit pattern might be covered is explained using drawing 1.

[0028] First, after forming the 1st silicon oxide film 2 and forming a circuit pattern 3 further on a silicon substrate 1, the 2nd silicon oxide film 4 was formed. In addition, the 1st silicon oxide film 2 is SiH<sub>4</sub>. Gas and O<sub>2</sub> Membranes are formed by the plasma-CVD method using gas by 500nm of thickness. Moreover, a circuit pattern 3 forms the aluminum-Si film in a spatter, and is formed in a predetermined pattern of a photolithography and etching. Furthermore, the 2nd silicon oxide film 4 is SiH<sub>4</sub>. Gas and O<sub>2</sub> Membranes are formed by the plasma-CVD method using gas by 100nm of thickness. However, this is the thickness in the part formed by the upper part of a circuit pattern 3, and serves as thin thickness from this in the narrow trench between circuit patterns 3.

[0029] Next, plasma treatment of the 2nd silicon oxide film 4 front face was carried out on condition that the following.

[0030] Plasma treatment condition installation gas : N<sub>2</sub>O Flow rate 200sccm pressure : 13.3PaRF power : 300W (13.56MHz)

wafer temperature: a room temperature -- by this, Si-O association of the 2nd silicon oxide film 4 front face was hydroxyl-group-ized, and became Si-OH.

[0031] next -- as a silane coupling agent -- 3, 3, 4, 4, 5, 5, 6, 6, and 6-nona FURORO hexyl trichlorosilane ( $\text{CF}_3$ ) ( $\text{CF}_2$ ) 3 2 ( $\text{CH}_2$ )  $\text{SiCl}_3$  It prepared, and the spin coat of what dissolved this in the carbon tetrachloride 1% of the weight was carried out to the above-mentioned wafer, and it was left at the room temperature for about 1 hour. In addition, thereby, the above-mentioned silane coupling agent carried out the chemical bond to the hydroxyl group of a silicon oxide film front face.

[0032] Then, the carbon tetrachloride washed this wafer and the superfluous unreacted silane coupling agent was removed.

[0033] And the organic compound insulator 5 which consists of amorphous Teflon (the Du Pont make, a trade name: Teflon AF) was formed at the thickness it is thin about 1 micrometer on the 2nd silicon oxide film 4 to which surface treatment was performed as mentioned above. In addition, in order to have formed this organic compound insulator 5, it was made to dissolve in a fluorocarbon system solvent (3 M company make, a trade name: FURORINATO), the coating whose viscosity is 30cp extent was prepared, and this coating was applied on the 2nd silicon oxide film 4 by performing a spin coat in rotational frequency 3000rpm. in addition, after [ spreading ], and controlled atmosphere:nitrogen gas, temperature:100 degree-C and pressure: -- an atmospheric pressure -- conditions -- for 2 minutes -- baking -- then, controlled atmosphere:nitrogen gas and temperature:260 degree C -- annealing treatment was performed on conditions.

[0034] Then,  $\text{SiH}_4$  Gas and  $\text{O}_2$  By the plasma-CVD method using gas, the 3rd silicon oxide film 6 of 500nm of thickness was formed.

[0035] Thereby, the circuit pattern 3 was covered with the 2nd silicon oxide film 4, an organic compound insulator 5, and the 3rd silicon oxide film 6. The cascade screen which consists of these silicon oxide film 4, an organic compound insulator 5, and the 3rd silicon oxide film 6 turns into an interlayer insulation film with a dramatically low dielectric constant by existence of an organic compound insulator 5. Moreover, since an organic compound insulator 5 consists of fluororesin, it excels also in thermal resistance.

[0036] Also in the gestalt of this operation, since the organic compound insulator 5 is formed through the silane coupling agent on the 2nd silicon oxide film 4, although this organic compound insulator 5 consists of fluororesin with a very large coefficient of thermal expansion more than glass transition temperature, the adhesive property over the 2nd silicon oxide film 4 is large.

[0037] As mentioned above, although the gestalt of the concrete operation which applied this invention was explained, this invention is not limited to what was mentioned above. For example, although both hydroxyl-group-izing of the front face of the silicon oxide film and spreading of a silane coupling agent of the gestalt of the 1st operation and the gestalt of the 2nd operation were performed, only either may be performed among hydroxyl-group-izing of the front face of the silicon oxide film, and spreading of a silane coupling agent.

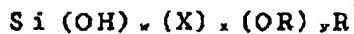
[0038] Moreover, it is  $\text{Ar}+\text{H}_2$  in order to hydroxyl-group-ize a silicon oxide film front face in the gestalt of above-mentioned operation. Although the plasma and the  $\text{N}_2\text{O}$  plasma were irradiated, instead of this, the processing and steam exposure by fluoric acid may be performed. What is necessary is to dip the wafer with which the silicon oxide film was formed about 10 seconds in an one-mol % fluoric acid solution, and for pure water just to wash for about 10 minutes, if processing by fluoric acid is performed. Moreover, what is necessary is just to put the wafer with which the silicon oxide film was formed to a steam under ordinary temperature and the environment which becomes the pressure of about 6700Pa, if steam exposure is performed.

[0039] Moreover, in the gestalt of above-mentioned operation, although what dissolved the silane coupling agent in the solvent was applied with the spin coat method in order to make a silane coupling agent hold on the silicon oxide film, the class of silane coupling agent, the class of solvent, and the concentration of a silane coupling agent can be changed suitably. For example, the concentration of a silane coupling agent can be preferably changed suitably in 0.2 - 4% of the weight of the range 0.01 to 30% of the weight. Moreover, the method of application may not be restricted to a spin coat method, either, but may be a dipping method, or you may be a vacuum deposition method.

[0040] You may be any as long as it is a compound as not restricted to what was shown in the gestalt of operation mentioned above as a class of silane coupling agent but shown in \*\* 3.

[0041]

[Formula 3]



(但し、w、x、y、zは整数であり、 $0 \leq w \leq 3$ 、 $0 \leq x \leq 3$ 、 $0 \leq y \leq 3$ 、 $1 \leq z \leq 3$

$w+x+y \geq 1$ 、 $w+x+y+z=4$ を満たす。)

また、Xはハロゲン、OR'はアルコキシル基を示す。

R'はアルキル基、ハロゲン化アルキル基、アルケン基、アミノアルキル基およびこれらの誘導体

より選ばれるいずれか1種を示し、 $z \geq 2$ のときは、これらの任意の組合わせとする。)

[0042] Specifically Trimethylchlorosilane, gamma-chloropropyltrimetoxysilane, Vinyl trichlorosilane, vinyltriethoxysilane, vinyltrimetoxysilane, A vinyl tris (beta-methoxyethoxy) silane, gamma-methacryloxypropyl trimethoxy gardenia fruit run, beta-(3, 4-epoxycyclohexyl) ethyltrimetoxysilane, Gamma-glycidoxypolytrimetoxysilane, gamma-mercaptopropyltrimetoxysilane, gamma-aminopropyl triethoxysilane, N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane, gamma-ureido propyl triethoxysilane, N-beta-(aminoethyl)-beta-aminopropyl methyl dimethoxysilane, etc. are known.

[0043] In addition, when using fluororesin as an organic material for forming an organic compound insulator, using what contains a fluorine atom as a silane coupling agent, it shall be suitable, at least one of the R' in the \*\*\*\*\*-izing 3 shall contain a fluorine atom, and it is suitable. concrete -- poly phloroalkyl trichlorosilane: (CF<sub>3</sub>) (CF<sub>2</sub>)<sub>n</sub> CH<sub>2</sub> SiCl<sub>3</sub>, poly phloroalkyl trimethoxysilane:(CF<sub>3</sub>) (CF<sub>2</sub>)<sub>n</sub> CH<sub>2</sub> Si(OCH<sub>3</sub>)<sub>3</sub>, and poly phloroalkyl trihydroxy silane:(CF<sub>3</sub>) (CF<sub>2</sub>)<sub>n</sub> CH<sub>2</sub> Si(OH) -- three etc. -- it is mentioned. However, n is two or more integers here. Moreover, 3, 3, and 3-truffe ROROPURO pill trichlorosilane, methyl - 3, 3, and 3-truffe ROROPURO pill dichlorosilane, 3, 3, 4, 4, 5, 5, 6, 6, and 6-nona FURORO hexyl trichlorosilane, Dimethoxymethyl - 3, 3, and 3-truffe ROROPURO pill run, 3 and 3, and 3-truffe ROROPURO pill trimethoxysilane, 3, 3, 4, 4, 5, 5, 6, 6, and 6-NONAFURORO hexyl methyl dichlorosilane, 3-TORIFURORO acetoxy propyltrimethoxysilane, etc. are usable.

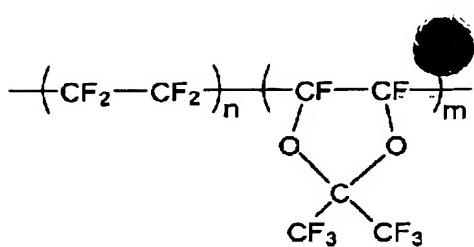
[0044] In the gestalt of the 1st operation, after applying such a silane coupling agent, although it was left at the room temperature for about 1 hour, 50-200 degrees C of reactions of the hydroxyl group of a silicon oxide film front face and a silane coupling agent may be promoted by heating at about 100 degrees C desirably.

[0045] Moreover, in the gestalt of above-mentioned operation, although it preceded for forming an organic compound insulator and the silane coupling agent was supplied to the front face of the silicon oxide film, a silane coupling agent may be supplied to the front face of the silicon oxide film at formation and coincidence of an organic compound insulator. The approach of applying the coating containing the ingredient and silane coupling agent of an organic compound insulator to the front face of the silicon oxide film as an approach of supplying a silane coupling agent to formation and coincidence of an organic compound insulator, the approach of carrying out vapor codeposition of a silane coupling agent and the ingredient of an organic compound insulator with a vacuum deposition method, etc. are mentioned. At this time, it is referred to as 1 / 1000 - 1/5, and is suitable, and it is a weight ratio and it is suitable, the ratio (a silane coupling agent/organic material) of a silane coupling agent and the ingredient of an organic compound insulator being especially used as 1 / 500 - 1/10. The effectiveness of raising the adhesive property of the silicon oxide film and an organic compound insulator becomes inadequate, if there are too few amounts of a silane coupling agent, and if reverse has too many amounts of a silane coupling agent, the film reinforcement of an organic compound insulator will deteriorate.

[0046] Furthermore, the organic material for forming an organic compound insulator is not restricted to what was mentioned above, either, for example, its polyimide system resin is also usable. The polyimide system resin film can be formed by spreading and heat treatment. In addition, polyimide may be denatured by a siloxane etc. in order to improve a heat characteristic. Moreover, the fluoride poly allyl compound ether as shown in SAITOPPU (Asahi glass company make, trade name) as shown in \*\* 5 besides Teflon AF (the Du Pont make, trade name) as shown in \*\* 4 also as fluororesin, and \*\* 6 etc. can be used. Each of these organic materials is applied by the spin coat method, and is suitable.

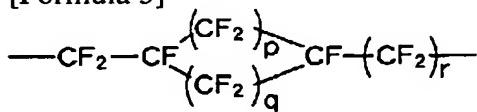
[0047]

[Formula 4]



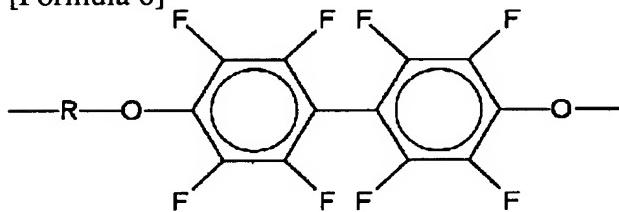
[0048]

[Formula 5]



[0049]

[Formula 6]



[0050] Moreover, an organic compound insulator may be formed by benz-cyclo-butene, the poly PARAKI silylene, etc., and membranes can be formed with a CVD method in this case. In addition, similarly that by which the fluorine was introduced into these compounds can be formed with a CVD method.

[0051] In addition, it sets in the gestalt of above-mentioned operation, and is membrane formation of the silicon oxide film SiH4 Gas and O2 Although carried out by the plasma-CVD method using gas, it is tetra-ethoxy silane (TEOS) gas and O2. You may carry out by the plasma-CVD method using gas etc.

[0052]

[Example] Here, in order to show the usefulness of this invention, it evaluated about the adhesive property of the organic compound insulator formed by carrying out like the gestalt of the 1st operation, and the gestalt of the 2nd operation.

[0053] experiment 1 -- here, it evaluates about the adhesive property of the organic compound insulator formed in the front face of the flat silicon oxide film as shown with the gestalt of the 1st operation. in addition, various classes of silane coupling agent and classes of ingredient of an organic compound insulator were boiled, and were changed here.

[0054] The wafer with which the silicon oxide film was specifically first formed on the substrate as the gestalt of the 1st operation showed is prepared, and it is this silicon oxide film front face Ar/H2 It hydroxyl-group-ized by the plasma treatment using mixed gas. And as (A) - (E) as shown in a table 1 was prepared as a silane coupling agent and the gestalt of the 1st operation of this showed, it applied to the front face of the silicon oxide film.

[0055]

[A table 1]

|                | 化学式   |
|----------------|---|
| シランカップリング剤 (A) | (CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>   |
| シランカップリング剤 (B) | CH <sub>2</sub> =CHSi(OCH <sub>3</sub> ) <sub>3</sub>   |
| シランカップリング剤 (C) | H <sub>2</sub> NCH <sub>2</sub> NHC <sub>2</sub> H <sub>5</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>                                |
| シランカップリング剤 (D) | CF <sub>3</sub> (CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> |
| シランカップリング剤 (E) | CH <sub>2</sub> =CHSiCl <sub>3</sub>  |

[0056] And the organic compound insulator which consists of a high molecular compound (a), a high molecular

compound (b), and a high molecular compound (c) was formed on the silicon oxide film with which the above silane coupling agents were applied, respectively.

[0057] In addition, a high molecular compound (a) is the polymethylmethacrylate of the Polyscience molecular weight 100000, a high molecular compound (b) is polyvinyl alcohol of the Polyscience molecular weight 25000, and high molecular compounds (c) are the Du Pont make and fluoroforesin which becomes trade name:Teflon AF160.

[0058] And that what is necessary is just to form the organic compound insulator which consists of a high molecular compound (a) as it was shown in the gestalt of the 1st operation, the organic compound insulator which consists of a high molecular compound (b) prepared the 2-% of the weight water solution of this high molecular compound (b), and formed it by applying this with a spin coat method on the above-mentioned silicon oxide film. In order to have formed the organic compound insulator which consists of a high molecular compound (c), this high molecular compound (c) was dissolved in the solvent (3 M company make, a trade name: FURORINATO) 2% of the weight, and this was applied with the spin coat method on the above-mentioned silicon oxide film. In addition, the solvent after spreading and in the film was fully removed.

[0059] The organic compound insulator which becomes the wafer with which surface treatment according to silane coupling agent (A) - (E) as mentioned above was performed from high-molecular-compound (a) - (c) obtained 15 kinds of sample wafers formed, respectively.

[0060] In addition, for the comparison, three kinds of above-mentioned organic compound insulators were formed, respectively also on the silicon oxide film which did not perform surface treatment by the silane coupling agent, and the sample wafer was obtained.

[0061] And the adhesive property of the silicon oxide film and an organic compound insulator was investigated as follows about a total of 18 kinds of above sample wafers.

[0062] That is, after establishing 100 blemishes of the square of 2mm around to the organic compound insulator of each sample wafer using a cutter knife, the above-mentioned organic compound insulator for a scratch counted the number which exfoliated from the silicon oxide film by making a commercial cellophane tape adhere and removing this cellophane tape.

[0063] The assessment result about each sample wafer is shown in a table 2.

[0064]

[A table 2]

|                | 高分子化合物 (a) | 高分子化合物 (b) | 高分子化合物 (c) |
|----------------|------------|------------|------------|
| シランカップリング剤 (A) | 4 3        | 4 5        | 6 7        |
| シランカップリング剤 (B) | 5 2        | 6 0        | 7 8        |
| シランカップリング剤 (C) | 3 3        | 2 6        | 5 2        |
| シランカップリング剤 (D) | 4 7        | 5 5        | 3 8        |
| シランカップリング剤 (E) | 4 8        | 3 8        | 7 3        |
| 表面改質なし         | 9 6        | 9 9        | 1 0 0      |

[0065] About the sample wafer produced without using a silane coupling agent, a table 2 shows that the organic compound insulator for a scratch almost exfoliates altogether, even if the high molecular compounds which constitute an organic compound insulator are any of (a) - (c). On the other hand, even if it combines any of silane coupling agent (A) - (E) and high-molecular-compound (a) - (c) in the sample wafer which carried out surface treatment of the silicon oxide film by the silane coupling agent, it turns out that exfoliation of an organic compound insulator can control substantially. That is, by carrying out surface treatment of the silicon oxide film by the silane coupling agent shows that the adhesive property of this silicon oxide film and an organic compound insulator is improved substantially.

[0066] In addition, when a silane coupling agent (A), (B), (C), and (E) are used, the organic compound insulator which consists of a high molecular compound (c) tends to exfoliate rather than the organic compound insulator which consists of a high molecular compound (a) and (b), but when a silane coupling agent (D) is used, the organic compound insulator which consists of a high molecular compound (c) has stopped being able to exfoliate easily rather than the organic compound insulator which consists of a high molecular compound (a)

and (b). It turns out that it is more desirable than this to apply beforehand to a silicon oxide film front face what faces to form the organic compound insulator which consists of fluororesin like a high molecular compound (c), and has the substituent which contains a fluorine atom like a silane coupling agent (D).

[0067] experiment 2 -- here, as the gestalt of the 2nd operation showed, adhesive assessment of an organic compound insulator was performed about the case where an organic compound insulator is formed on the wafer with which the silicon oxide film was formed so that a circuit pattern might be covered and which has detailed irregularity.

[0068] The sample wafer was produced by making it concrete as the gestalt of the 2nd operation showed, hydroxyl-group-izing the front face of the 2nd silicon oxide film 4 which covers a circuit pattern 3 by the plasma treatment using N<sub>2</sub>O gas, forming the organic compound insulator 5 which consists of Teflon AF (the Du Pont make, trade name), and forming the 3rd silicon oxide film 6 further. This is made into sample wafer (b).

[0069] Moreover, the sample wafer was produced like the gestalt of the 2nd operation except having formed the organic compound insulator 5 which consists of other fluororesin:SAITOPPU (Asahi glass company make, trade name), FLARE (Allied-Signal, Inc. make, trade name), and polyimide fluoride instead of Teflon AF (trade name) in the thickness it is thin 500 nmms. In addition, with these fluororesin having been shown in the gestalt of the 2nd operation, similarly, it is made to dissolve in a solvent and is applied by the spin coat method, and annealing temperature is changed into 350 degrees C although formed by performing baking and annealing. That a sample wafer (Ha) and whose ingredient of an organic compound insulator 5 are polyimide fluoride about that whose ingredient of sample wafer (\*\*) and an organic compound insulator 5 is FLARE (trade name) about that whose ingredient of an organic compound insulator 5 is SAITOPPU (trade name) is made into sample wafer (d).

[0070] Furthermore, sample wafer (e) was produced like the gestalt of the 2nd operation except having formed the organic compound insulator 5 which consists of poly PARAKI silylene, without applying a silane coupling agent, after hydroxyl-group-izing the front face of the 2nd silicon oxide film 4. Here, using a common low pressure CVD system, the JIPARA xylylene is made to sublimate at 200 degrees C, it decomposes into a xylylene monomer at 650 degrees C, and the organic compound insulator 5 which consists of poly PARAKI silylene is formed by supplying, where this is heated at 150 degrees C.

[0071] Moreover, sample wafer (\*\*) in which it comes to form an organic compound insulator was produced, without [ without it hydroxyl-group-izes a silicon oxide film front face for a comparison, and ] applying a silane coupling agent. First, as shown in drawing 2, specifically, the 2nd silicon oxide film 104 was formed so that the circuit pattern 103 formed on the 1st silicon oxide film 102 on a silicon substrate 101 might be covered. And without applying a silane coupling agent, without hydroxyl-group-izing this 2nd silicon oxide film 104 front face, Teflon AF (trade name) was applied, and the organic compound insulator 105 was formed, then the 3rd silicon oxide film 106 was formed. In addition, the formation approach of an organic compound insulator 105 etc. presupposed that it is the same as that of the gestalt of the 2nd operation.

[0072] And it investigated whether the void would have occurred in the organic compound insulator 5,105 about each sample wafer (b) - (\*\*).

[0073] Consequently, in sample wafer (b) - (e), as shown in drawing 1, the void had not generated the narrow trench section between circuit patterns 3 in an organic compound insulator 5, either, but in sample wafer (\*\*), as shown in drawing 2 R> 2, it turned out that the void has occurred in the organic compound insulator 105 of the trench section between circuit patterns 3.

[0074] In sample wafer (b) - (e), since the adhesive property of the 2nd silicon oxide film 4 and the ingredient of an organic compound insulator 5 was enough, this shows that the ingredient of an organic compound insulator 5 did not need to separate from the 2nd silicon oxide film 4, even if thermal expansion happens with heating for removing a solvent at the time of formation of an organic compound insulator 5.

[0075] That is, hydroxyl-group-izing the front face of the 2nd silicon oxide film 4 or by applying a silane coupling agent further showed that the adhesive property of the 2nd silicon oxide film 4 and an organic compound insulator 5 could be raised.

[0076]

[Effect of the Invention] An adhesive property with the insulator layer which consists of this silicon oxide film and an organic material formed on this improves by [ which hydroxyl-group-ize the front face of the silicon

oxide film with the application of this invention ] depending especially and/or making a silane coupling agent hold on the front face of the silicon oxide film so that clearly also from the above explanation. [0077] Thereby, the dependability of the semiconductor device using the organic material film as a component can improve, and the applicability of the organic material film can be expanded. [0078] For this reason, even if it faces using the organic material of a low dielectric constant as an interlayer insulation film which can reduce wiring capacity, dependability improves substantially.

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[Translation done.]

**\* NOTICES \***

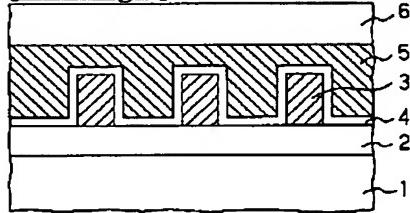
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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

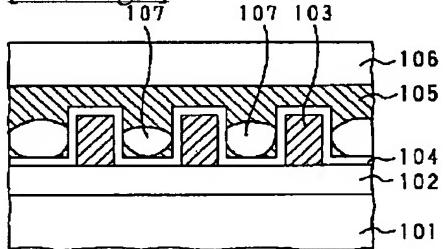
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**DRAWINGS**

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**[Drawing 1]**

3: 斧線パターン  
4: 第2の硬化シリコン膜  
5: 有機絶縁膜

**[Drawing 2]**

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[Translation done.]

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